SEGMENTAL DYNAMICS OF BULK POLY(VINYL ACETATE)-d_3 BY SOLID-STATE ^{2}H NMR: EFFECT OF SMALL MOLECULE PLASTICIZER

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Supporting Information

Jump Rate Bar Graphs. A more detailed representation of the distribution of jump rates for PVAc as a function of plasticizer content and temperature is given in **Figure A1**. This figure has bar heights that indicate the weighting factors of the simulated spectra plotted against the jump rates used to fit the experimental spectra. As the temperature increases, the distribution of the jump rates shifts steadily from the slow to the intermediate regime. In general, most of the spectra used in the basis set contributed little or nothing to individual fits and their contributions are not shown. At a given temperature, the contributions in the simulated spectra from the intermediate components increased as the amount of plasticization increased. At higher temperatures, there was a moderate contribution from the faster jump rate components.

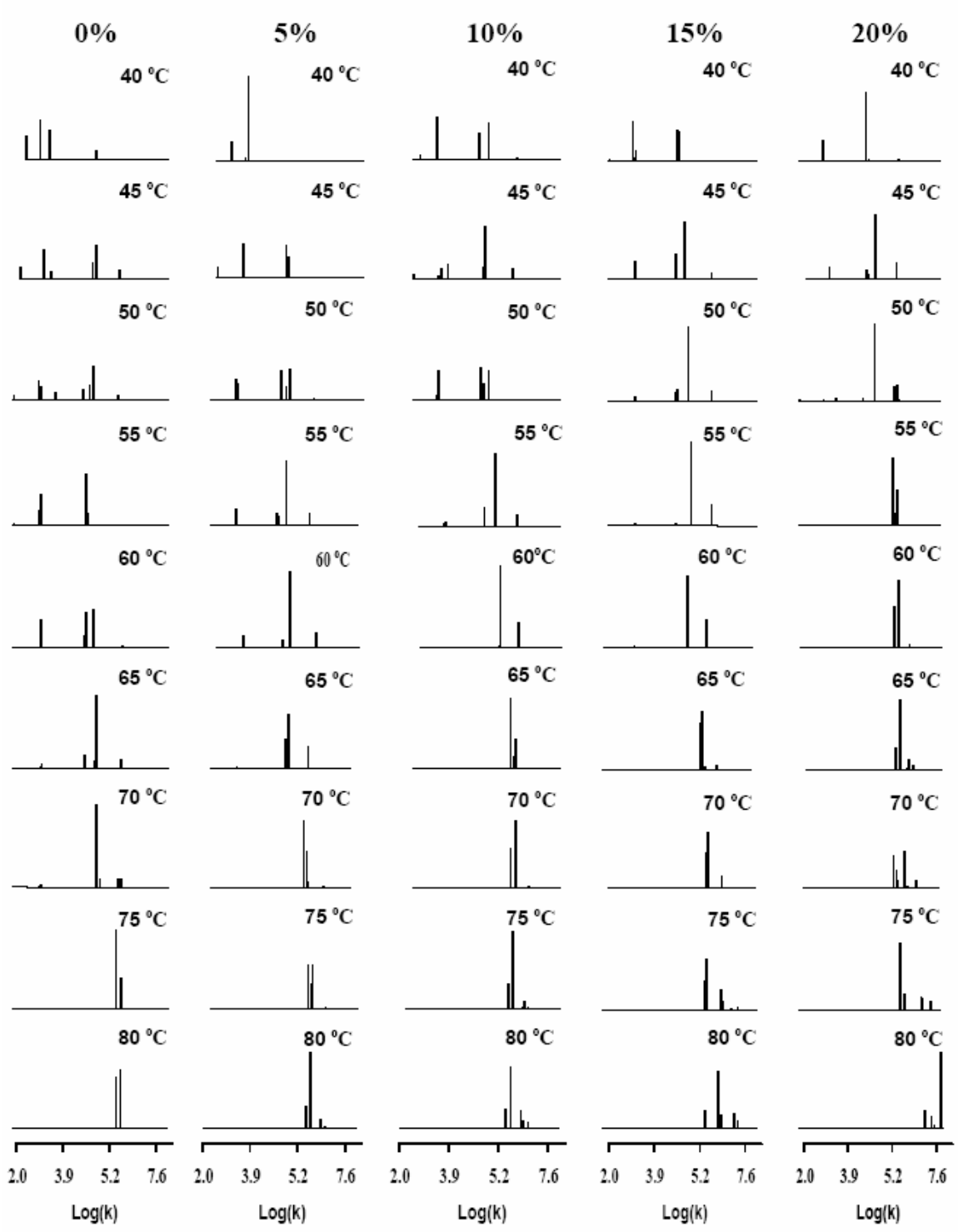

Figure A1. Distributions of jump rates from the simulations for each sample (0, 5, 10, 15, 20% plasticizer) at different temperatures.

Log $<\tau_c>$. The average correlation times, $<\tau_c>$s, were calculated for each sample from the master correlation function curves for each spectrum. A plot of the log$<\tau_c>$ for the different samples as a function of temperature is shown in **Figure A2**. It should be noted that the NMR line shapes are not particularly sensitive to motions in either fast (log τ_c < -6.8) or slow (log τ_c > -4.5). The average correlation times are also dominated by the longer correlation time values. This results in the apparent flattening in the long and short correlation time range. The correlation times decreased, as expected, with increases in temperature or increases in plasticizer content. Values of the parameter β were in the range of 0.21 to 0.34 and increased with increasing temperature.

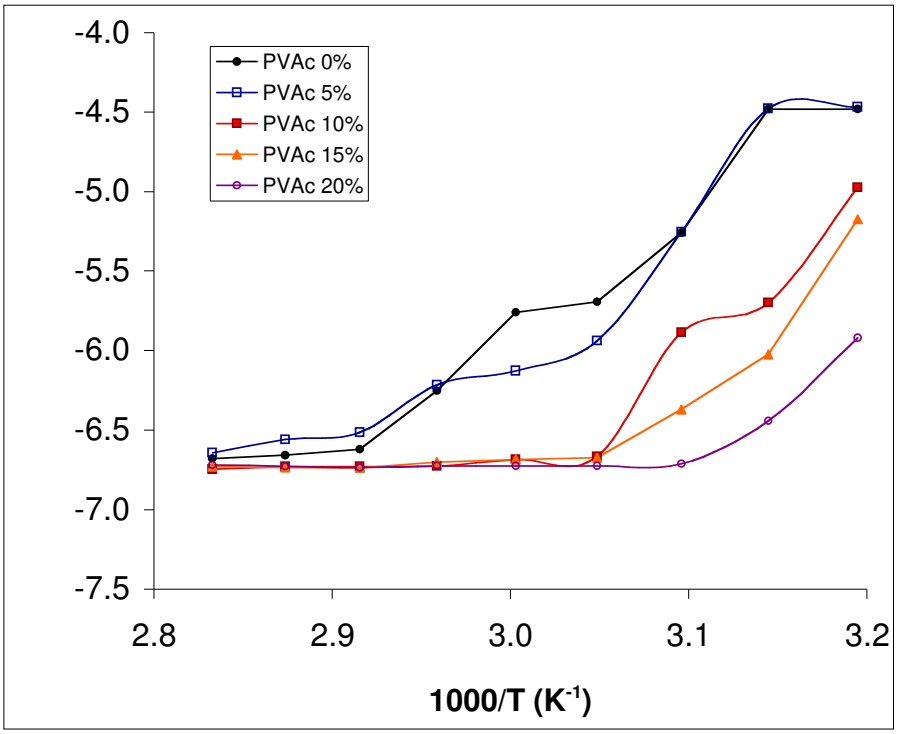

Figure A2. Log correlation times as a function of temperature for the different plasticized (0, 5, 10, 15, 20% plasticizer) samples.

Shifting of <log k> Data with WLF Parameter. In order to further test the validity of the WLF approach to the NMR data, the shift factor, C_2 (= 46.8 °C) was applied to the temperature scale for the <log k> values. This resulted in the replacement of $1/T$ with $1/(T + C_2 - T_g(\%p))$, where $T(\%p)$ is the glass transition temperature at the appropriate plasticizer content. The resultant plot is shown in Figure A3 with the line representing the average of the different data sets. It can be observed that the data superimpose well.

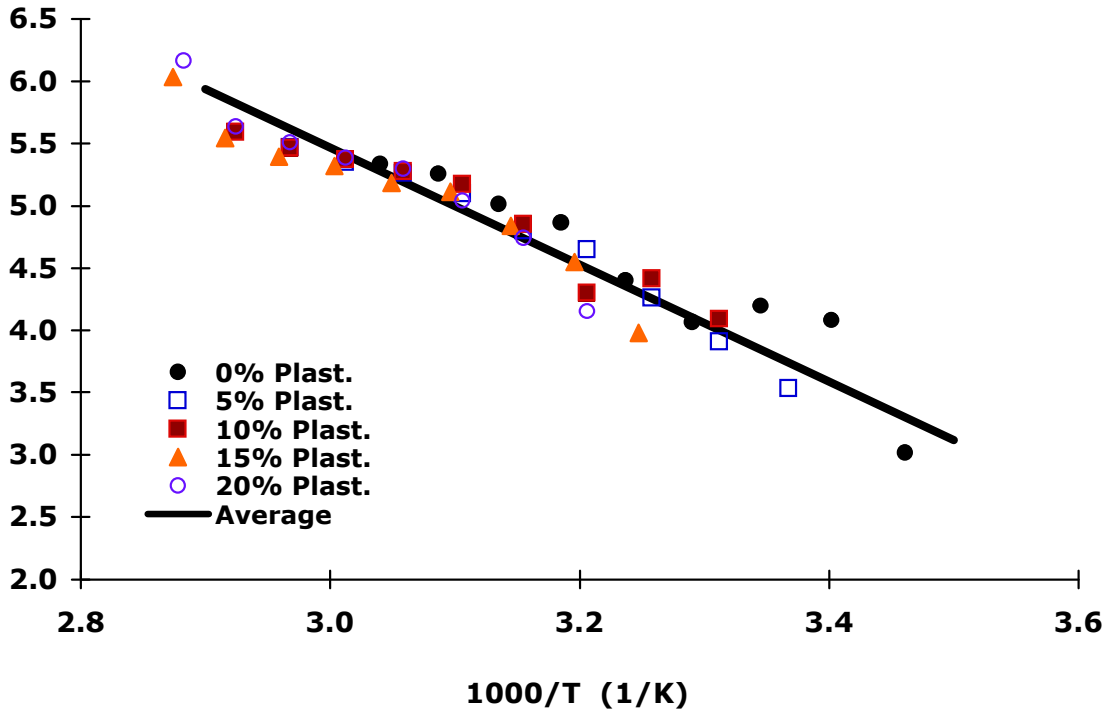

Figure A3. The average of the log of jump rates as a function of reciprocal temperature. The data are shifted by the C2 from the WLF equation.